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PHOTODECOMPOSITION OF WATER OVER PT/TIO2 CATALYSTS.(U)

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⁶ Photodecomposition of Water over Pt/TiO₂ Catalysts.

by

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Photodecomposition of Water over Pt/TiO₂ Catalysts (a)

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Abstract

We report experiments demonstrating that the decomposition of water is catalytic at 23°C when a platinized, powdered titanium dioxide catalyst, illuminated with band-gap radiation, is used.

I. Introduction.

The photoassisted decomposition of H₂O in photoelectrochemical (PEC) cells has recently received attention as a potential solar energy conversion and storage system [1-3]. Heterogeneous catalysts have some general advantages as compared to PEC cells because they are less expensive to construct and because they can be made with large surface areas. However, these advantages can not be realized until photocatalytic activity is demonstrated. The heterogeneous photocatalytic decomposition of gas phase H₂O has been reported by Schrauzer and Guth [4], who detected H₂ and O₂ in the ratio of 2:1 when TiO₂ or Fe₂O₃-doped TiO₂ was equilibrated with H₂O vapor and illuminated by UV light in an Ar atmosphere. The H₂ and O₂ formation was, however, much slower than in PEC cells, and after a few hours, the rate dropped to almost zero. They ascribed the rate loss to the back reaction. This experiment has been repeated by Van Dams and Hall [5] using a flow system in order to determine the steady-state photocatalytic activity of TiO₂. After 6 hours of UV illumination and product collection, only a trace of H₂ was detected. Based on this result they concluded that any observed H₂ production on TiO₂ is not catalytic and probably arises from the photodecomposition of the hydroxylated surface typically found on TiO₂ [6].

Metallized semiconductors often show different selectivities in heterogeneous photocatalytic reactions than semiconductors alone. For example, Kraeutler and Bard [7] have shown that platinized TiO₂ catalyzes the decomposition of liquid acetic acid selectively to methane under UV illumination. However, in a PEC cell using TiO₂ as the photoanode, the products are dominated by ethane. Bulatov and

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Khidel [8] have claimed the photodecomposition of water ($1\text{ N H}_2\text{SO}_4$) in the presence of platinized TiO_2 .

We report here studies of reactions of H_2O over TiO_2 and platinized TiO_2 (Pt/TiO_2) and find no evidence of catalytic activity for water decomposition in the former case while in the latter measurable catalytic activity is found when Pt/TiO_2 is wet. Isotopically labelled water, H_2^{18}O and D_2O , were used to establish some features of the mechanism.

II. Experimental.

Reactions were carried out in an evacuable, closed circulation system (180 ml volume) linked to a mass spectrometer. The reaction cell was made of quartz, and during reaction, its temperature was maintained at 23°C by a water bath. The catalyst (0.25 g) was spread uniformly on one face of the reaction cell and outgassed at 200°C for 3 hr. After introducing reactants, it was illuminated by a 200W high-pressure mercury lamp that was filtered through a quartz cell filled with NiSO_4 solution to remove infrared. The gas mixture was sampled at various times, and after passage through a cold trap at about -110°C to remove H_2O , was analyzed by the mass spectrometer.

TiO_2 (anatase) was obtained from MCB and platinized TiO_2 (~2 wt% Pt) was prepared by the photodecomposition of hexachloroplatinate dissolved in a Na_2CO_3 -acetic acid buffer solution [9]. The total surface area was about $11\text{ m}^2\text{gm}^{-1}$. Oxygen-18 H_2O (99.3%) was obtained from Prochem and D_2O (99.8%) from Clinechem. Distilled H_2O (or the above isotopic compounds), outgassed several times at dry-ice temperature, was introduced as a gas into the reaction vessel at 24 torr, the room temperature vapor pressure (we refer to this catalyst as "dry"). In some experiments the catalyst was cooled to 0°C during H_2O admission in order to enhance the amount of water adsorbed (we define this as a "wet" catalyst since a liquid-vapor equilibrium was established after warmup to 23°C).

III. Results and Discussion.

The TiO_2 sample was variously pretreated: (1) Calcined in air at 1000°C for 2 hr as recommended by Schrauzer and Guth[4], (2) reduced (doped) in a H_2 stream at temperatures between 500 and 750°C for 3-10 hr and (3) no pretreatment. None of these TiO_2 samples were active for the photocatalyzed production of H_2 and O_2 from H_2O in either the dry or the wet state. In the case of strongly doped TiO_2 , only H_2 was formed under UV illumination and the maximum amount was about 3×10^{-7} mole (about 10^{17} molecules m^{-2}). Hydrogen formation was not affected by the presence of N_2 or CO but was completely retarded by the addition of 3×10^{-2} torr of O_2 . These results suggest that H_2 is formed by the non-catalytic reaction of H_2O with a strongly reduced form of TiO_2 , such as TiO [10]. Such a reaction could increase the surface OH concentration and it is not unreasonable to expect a change on the order of 10^{17} - 10^{18} m^{-2} [6]. This would account for all of the observed H_2 .

Dry, platinumized TiO_2 , prepared from TiO_2 doped in H_2 at 700°C for 6 hr, also produced H_2 in the presence of gas phase H_2O under UV illumination, with concomitant formation of CO_2 and a small amount of CH_4 [11], but no O_2 was observed. This H_2 is thought to form in the same way as for strongly doped TiO_2 alone (see above). When a fresh Pt/TiO_2 sample was illuminated in vacuum (3×10^{-7} torr), no detectable products were formed. This suggests that, in the absence of H_2O , hydroxyls present on TiO_2 are not decomposed by UV light.

When Pt/TiO_2 was outgassed at 200°C for 2 hr, wet at 0°C with enough H_2O (0.2 ml) to cover its surface, and irradiated by

UV light at 23°C , H_2 and O_2 were formed in the ratio of nearly 2:1 (See Fig. 1). The initial rate of H_2 formation was 3.5×10^{-7} mole/hr but decreased to about 1×10^{-7} mole/hr after 2 hrs of irradiation. As a check on the source of this decline in the rate, the light source was turned off after 130 min (Fig. 1). Over the next 40 min, H_2 and O_2 were slowly consumed. When the light source was turned on at 170 min, the H_2 and O_2 pressures rose again. These results clearly point to the back reaction of H_2 and O_2 on Pt as the source of the declining net rate of H_2 and O_2 evolution. The rate of the back reaction is much slower than on dry Pt/TiO_2 probably because it is diffusion-controlled in the wet system. As shown in Fig. 2, when H_2^{18}O was used H_2 and $^{18}\text{O}_2$ were formed. A small amount of C^{18}O_2 was also formed. The amount of $^{18}\text{O}^{16}\text{O}$ formed was about 2% of $^{18}\text{O}_2$ and no $^{16}\text{O}_2$ was observed. The C^{18}O_2 formation is ascribed to the oxidation of a variable amount of adsorbed carbon present as a result of the decomposition of acetic acid during the preparation of catalyst. As a result, the H_2/O_2 ratio in Figs. 1 and 2 is slightly greater than 2. This result clearly shows that under conditions where H_2 , O_2 and CO_2 are formed, the oxygen is derived from H_2O , not from surface OH present at the beginning of the reaction. A separate experiment shows that oxygen isotope exchange is slow. When D_2O was substituted for H_2O , the products were D_2 , O_2 and a small amount of HD. No strong conclusions can be drawn from this data since D for H exchange at the surface is relatively fast.

In repeated experiments with the same catalyst, the time evolution of H_2 was reproducible to within $\pm 5\%$ as long as the

products were evacuated for only a short time. However, the activity slowly declined if extensive evacuation was done at room temperature or 200°C. Apparently the catalyst is poisoned but the mechanism is unknown.

Figure 3 shows that the rate dropped by about a factor of two when the catalyst was cooled to 0°C by an ice-water mixture; the apparent activation energy is estimated to be 5 kcal/mole. The use of a 415 nm-cut-off filter completely stopped the reaction, (Fig. 4) while a Plexiglass filter (380 nm cut-off) suppressed the rate to less than 1/20 and a Pyrex glass filter (275 nm cut-off) had little effect. The energy efficiency during the initial stages of the water decomposition reaction is roughly 5×10^{-4} . It is also noteworthy that Pt/TiO₂ prepared from undoped TiO₂ is much less active than Pt/H₂-doped TiO₂.

After the total amount of H₂ formed in the present experiments exceeded 10⁻⁵ mole the catalyst still showed significant activity for the photodecomposition of H₂O. This is additional evidence that the photolysis of H₂O on Pt/TiO₂ is catalytic. If only initially present surface OH groups on TiO₂ were photodecomposed, the amount of H₂ should never exceed 9×10^{-6} mole because the Pt/TiO₂ outgassed at 200°C has at most 4.4×10^{19} OH/g, which was determined by hydrogen exchange between D₂ and the surface OH groups.

The mechanism of the present process is not understood but probably involves features similar to those of PEC cells or Schottky barrier type photochemical diodes [12], in which Pt functions as a cathode and TiO₂ as a photoanode. Differences do exist, however,

since the operation of a Pt-TiO₂ PEC cell requires some external electrical potential in addition to band-gap radiation to decompose H₂O [2] while the Pt/TiO₂ powder catalyst works using only light. The Schottky barrier at a Pt-TiO₂ interface may play an important role in electron-hole separation.

IV. Summary and Conclusions.

These results demonstrate that the thermally uphill water decomposition reaction can be driven at 23°C using band-gap illumination of a Pt/TiO₂ powder covered with liquid water. As H₂ and O₂ accumulate, the back reaction becomes important and a photostationary state is reached. Isotopic labelling experiments show that liquid phase water is utilized and total yield measurements confirm that the products are not limited to a stoichiometric reaction of hydroxyl groups initially present at the surface. In the case of dry catalysts where small amounts of H₂ and no O₂ are formed, it is not clear whether the basic mechanism changes or the back reaction dominates. The mechanism, in either case, is not well-understood and many experiments must be done involving other catalysts, reactants and conditions. Some of these have been done or are underway in our laboratory. For example, the water-gas shift reaction [13] and the reactions of ethylene [14], and Texas lignite [15] with gas phase water are photocatalytic.

V. Acknowledgement.

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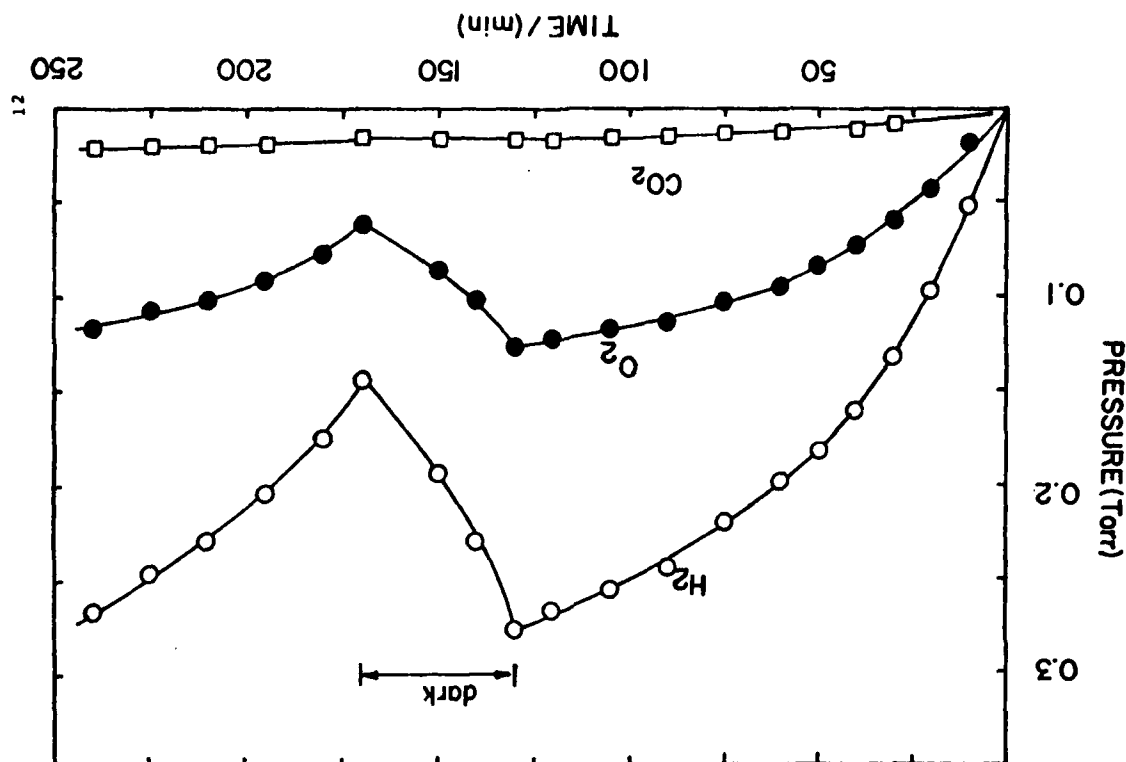
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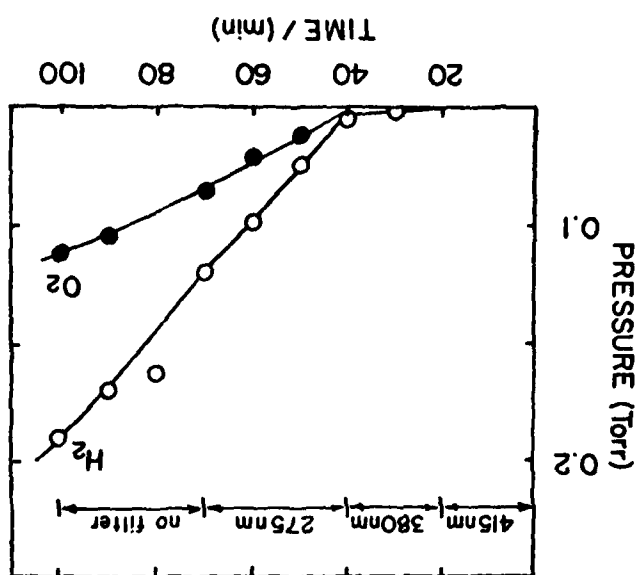
Figure 1. Time dependence of H_2 , O_2 and CO_2 production in a system comprised of Pt/TiO_2 , $H_2O(l)$ and band gap radiation at $23^\circ C$. During the period 130-170 min, the light source was off.

Figure 2. Time dependence of H_2 and $^{18}O_2$ production over an illuminated Pt/TiO_2 catalyst wet with $H_2^{18}O$ at $23^\circ C$. During the period 180-220 min, the light source was off.

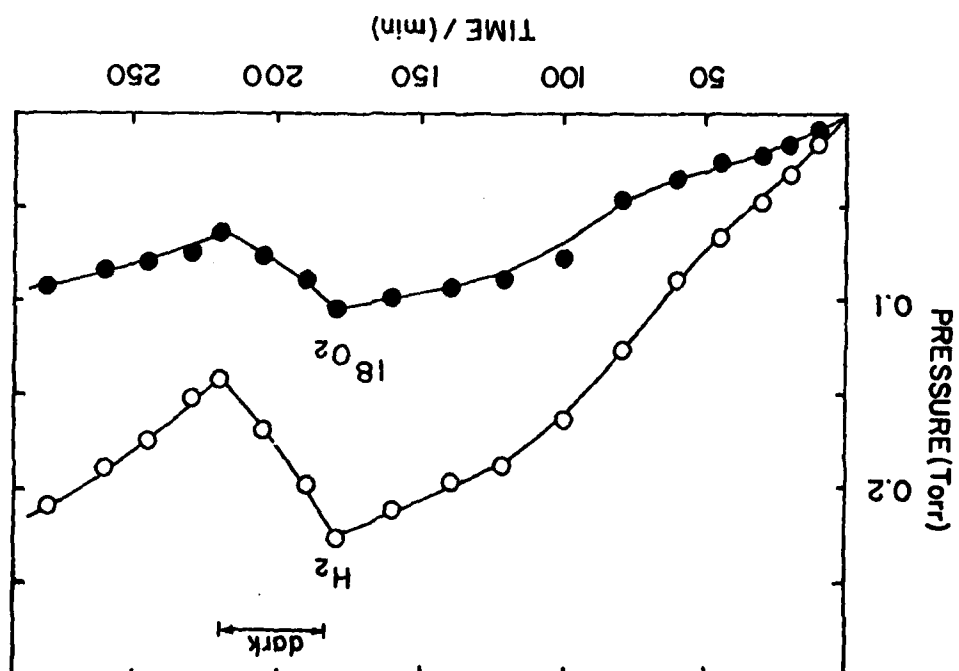
Figure 3. Time dependence of H_2 and O_2 production at 0 and $23^\circ C$.

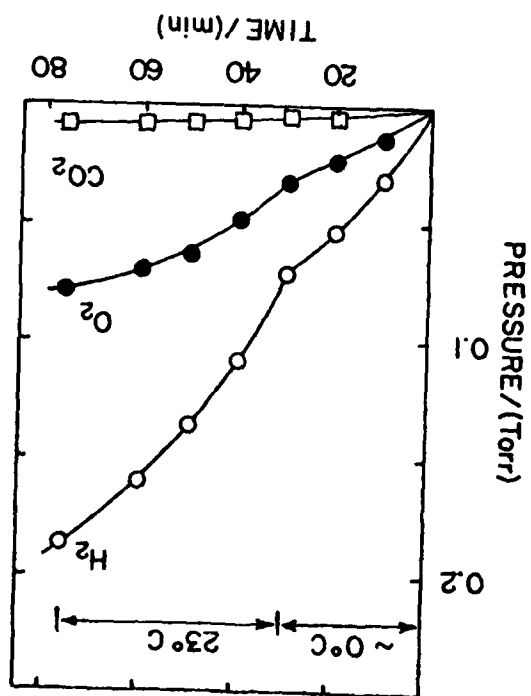
Figure 4. Effect of cut-off filters on the production of H_2 and O_2 from a wet, illuminated Pt/TiO_2 catalyst at $23^\circ C$.





Sato and White, Fig. 2





Safe and useful, Fig. 3